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(71) Applicant: Resem S.p.A., 31, Foro Buonaparte,
I-20121 Milan (IT)

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(72) Inventor: Trovati, Aldo, 1, via Borsi, Novara (IT)

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(74) Representative: Whalley, Kevin et al, Marks &
Clerk 57/60 Lincoln's Inn Fields, London WC2A 3LS (GB)

(54) **Process for producing aqueous dispersions of polyurethanes.**

(57) A mixture of a diol containing ionizable groups and of a polyol-polyester or polyol-poly ether is reacted with an aromatic or aliphatic or cycloaliphatic isocyanate, thereby obtaining a prepolymer with terminal isocyanic groups. The latter is reacted with a hydroxy-alkyl-acrylate or -methacrylate, so as to obtain an oligo-urethane having unsaturated terminal groups. The thus obtained product, after having been subjected to saponification, dispersed in water and subjected to polymerization in the presence of a radical catalyst, gives rise to a stable aqueous dispersion of polyurethane, suitable for forming coating films, or for use as a dressing or adhesive.

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"Process for Producing Aqueous Dispersions
of Polyurethanes"

This invention relates to a process for producing aqueous dispersions of polyurethanes.

The presently known operative processes for producing stable aqueous solutions of polyurethanes 5 are various; many such processes are described in the patent and bibliographic literature, see for instance D. Dieterich, Progress in Organic Coatings, 9, 281 (1981).

Such aqueous dispersions are nearly all of ionomeric type, i.e. they contain inside the polyurethanic 10 macromolecule some hydrophilic centers of ionic type, which act as internal surfactants and make the polymer dispersable or soluble in water.

The introduction of such ionic centers is carried out by employing particularly diols containing groups 15 which can be salified and which do not react or react only with difficulty with the isocyanic groups.

The ionic charge of the polyurethane depends on the nature of these diols: for instance with tertiary dialkanolamines and subsequent quaternization with organic or inorganic acids, hydrodispersed polyurethanes are 20 obtained having cationic nature; by using diols containing a carboxylic or sulphonic or phosphoric group, after salification, polyurethanic dispersions are obtained having anionic nature.

25 The preparation methods may be of solvent type,

2.

that is to say the polyurethane, before its dispersion in water, is obtained in solution of an organic solvent, that is inert towards the free isocyanic groups, such as acetone, methylketone, dioxane, or tetrahydrofuran,
5 which at the end of the preparation is removed by distillation.

The amount of organic solvent is generally very high, from 1 to 3 times the weight of the polyurethane, considered as dry, and therefore it is apparent that such
10 a process presents some drawbacks when applied on an industrial scale. Such drawbacks are low productivity per unit of available volume, necessity of rectifying the recycle solvent owing to its high water content, and long preparations times owing to the low temperature which
15 can be reached and owing to the distillation operations.

Methods which allow a sensible reduction in the organic solvent are described in the patent literature; for instance in U. S patent No. 4,183,836 it is disclosed that a polyisocyanic polymer also containing carboxylic
20 groups is dispersed in an aqueous solution containing a tertiary amine, that acts as salification agent, and a diamine that acts as chain lengthening agent, by acting on the isocyanic terminal groups of the prepolymer, thereby obtaining an ionic polyurethane-polyurea dispersed
25 in water.

In German patent No. 2,725,589 it is disclosed that a polyisocyanic prepolymer containing ionic groups is

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mixed, under anhydrous conditions, with diamines blocked by ketones (ketonimines) which are inert towards the isocyanic groups; the subsequent addition of the water hydrolyzes the ketoniminic groups to aminic groups, and therefore the free diamine is formed again, which acts as a chain lengthening agent, as in the previously mentioned U.S. patent No. 4,183,836.

In European patent No. 4069 it is disclosed that the lengthening (elongation) of the polyisocyanic prepolymers containing ionic groups is carried out after mixing, under anhydrous conditions, with hydrazines blocked by ketones (ketonhydrazines) and subsequent addition of water; the mechanism of the subsequent reactions is similar to those previously described.

In U.S. patent No. 3,756,992 another preparation method is described, according to which a polyisocyanic prepolymer containing ionic and/or ionizable centers is previously converted into a prepolymer with ureic terminal groups ($-\text{NH}-\text{CO}-\text{NH}_2$) by reaction with urea, by working at high temperature in order to maintain the prepolymer in the method state. After its dispersion in water, on such a prepolymer, methylolic groups are introduced on the ureic terminal groups or also on the NH-groups of the preformed urethanic groups, by means of formaldehyde in aqueous solution or by means of formaldehyde releasing compounds. By subsequent self-condensation of the formed methylolic groups, polyurethanes with a high molecular weight are obtained.

By using methods based on the water dispersion of ionized and subsequently lengthened (extended) polyisocyanic prepolymers with free or differently blocked diamines and/or hydrazines, essentially linear polyurethanes-polyureas are obtained and such methods can be easily applied by employing polyisocyanic prepolymers based on aliphatic isocyanates. On the contrary, with aromatic prepolymers the high reactivity of the isocyanic groups towards the water involves problems of foaming of the bulk and of formation of coagula, which cannot be dispersed again. On the other hand, the methods based on the condensation of the ionomeric methylated polyurethanes, although they allow the obtaining of reticulated structures and, consequently, film having high resistance towards the solvent, present the drawback that they give rise to finished products which always contain traces of free formaldehyde, with a very sharp odour and, above all, they release to the environment amounts of formaldehyde previously linked as methylollic or methylol-ether groups, in addition to the free formaldehyde, during the application steps, which in nearly all the processes require a thermal treatment.

Therefore, the present invention aims to provide a process for obtaining polyurethanic dispersions that can be easily realized either with aromatic, aliphatic or cycloaliphatic organic isocyanates; furthermore, according to such process, no organic solvent or only a small quantity thereof should be used during the

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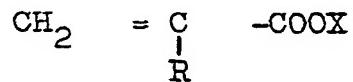
polyurethane preparation, reticulated macromolecular structures should be obtained, and highly irritating and dangerous decomposition products such as formaldehyde should not be released to the environment.

5 The present invention provides a process for producing stable aqueous dispersions of polyurethanes containing in the macromolecule hydrophilic ionic groups, as internal surfactants, either of anionic or cationic nature, which are present in amounts of 10-60 meq/100 g
 10 of dry polyurethane, the process being characterized by
 10 the following steps:

a) a mixture of a diol containing ionizable groups, which can be converted into hydrophilic anionic or cationic groups, and of an essentially linear macro-glycol, having a molecular weight of from 500 to 5000,
 15 of polyol-polyether and/or polyol-polyester type, is reacted at a temperature not higher than 100°C with an excess of a diisocyanate, thereby obtaining a pre-polymer containing free isocyanic groups:

20 b) the polyisocyanic prepolymer is then converted into oligo-urethane containing vinyl terminal unsaturated groups, by reaction with a compound containing hydroxyl radicals, which are reactive towards the isocyanic group, and having the general formula:

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where R is H or CH_3 , and X is a hydroxyalkyl radical;

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- c) the obtained oligo-urethane is subjected to salification in order to convert the ionizable groups into hydrophilic cations or anions, respectively of quarternary ammonium type or of carboxylic, sulphonic or phosphonic group type;
- d) the oligo-urethane containing the hydrophilic cationic and anionic groups is subjected to polymerization treatment of the terminal unsaturated groups, in an aqueous dispersion, in the presence of a radical catalyst at a temperature not higher than 100°C, so as to obtain an aqueous dispersion of polyurethane having a pre-established reticulation degree, that can be regulated by means of an optional addition of comonomer present in the polymerization step.
- According to the present invention, the polyurethane is obtained through the formation of a polyisocyanic prepolymer by reacting an organic diisocyanate and a mixture consisting of a macroglycol and a diol containing ionizable groups, suitably in such a quantity that the molar ratio between the isocyanic and the sum of the hydroxyl groups of the macroglycol and of the diol is from 1.2:1 to 2:1, preferably 1.5:1.

It is also possible to introduce triols having a low molecular weight, the quantity of which, however, is critical for the purpose of inducing the formation of prepolymers with a viscosity that can be easily treated in conventional apparatus. Furthermore, for the purpose of inducing the formation of more reticulated macro-

7.

molecular structures, such small quantities of triols have practically no influence.

The polyisocyanic prepolymer is then converted into oligo-urethane containing terminal unsaturated 5 functional groups of acrylic and/or methacrylic nature, by reaction with a hydroxy-alkyl-acrylate or a hydroxy-alkyl-methacrylate. The amount of such compound containing at least one hydroxyl group and at least one unsaturated ethylenic grouping depends on the content of 10 isocyanic free groups still present in the polyisocyanic prepolymer, so that the ratio between the -NCO groups of the polyisocyanic prepolymer and the -OH groups of the hydroxylated unsaturated compound, i.e. the eq-NCO/eq-OH ratio, is preferably from 0.5:1 to 1.1:1, more preferably 15 1:1.

The formation of the polyisocyanic prepolymer and its subsequent transformation into oligo-urethane with terminal ethylenic unsaturation can be carried out in the complete absence of organic solvent. The reaction tem- 20 peratures to obtain the various polyisocyanic prepolymers are almost always lower than 100°C, preferably from 50° to 90°C; the subsequent reactions with the compounds containing at least one hydroxyl group and an ethylenically unsaturated grouping are carried out at temperat- 25 ures lower than 150°C, preferably from 60° to 120°C.

The reactions can be carried out in the presence of known catalysts such as the tin-organic compounds or the tertiary amines; however, this is not generally necessary

8.

and it is preferable to carry out the reaction without a catalyst.

The essentially linear macroglycols, which can be utilized to form the oligo-urethane, have a molecular weight from 500 to 5000, preferably from 800 to 3000, and are of the saturated polyester, polyether, polyester-urethane type.

Examples of polyesters are the products of polycondensation of bicarboxylic, preferably aliphatic, acids or anhydrides, having from 4 to 9 carbon atoms with aliphatic diols having from 2 to 8 carbon atoms, alone or in mixture among them, or the polycondensation products on diolic "starters" of ϵ - caprolactam.

Examples of polyester-urethanes are the products of polyaddition of the above mentioned polyesters with organic diisocyanates in molar defect.

Examples of polyethers are the various types of polyethyleneglycol, polypropyleneglycol and, preferably, the polymerization products of tetrahydrofuran.

Examples of polyols with low molecular weight, which may be used in small quantities together with the above mentioned macroglycols, are preferably of trifunctional kind, such as trimethylpropane, glycerol and 1,2,6-hexanetriol.

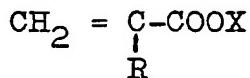
The employable organic diisocyanates may be either of the aromatic, aliphatic or cycloaliphatic type, but the aliphatic or cycloaliphatic diisocyanates are preferred, when high resistance against UV radiation

9.

and against hydrolytic degradation are desired.

Examples of suitable diisocyanates are 2,4-toluene-diisocyanate, alone or in mixture with the 2,6-toluene-diisocyanate isomer, 4,4'-diphenyl-methanediisocyanate,
 5 4,4'-dicyclohexyl-methanediisocyanate, 1-isocyanate-3, isocyanate-methyl-3,5,5-trimethylcyclohexane (or isophoronediisocyanate), and 2,2,4-trimethylhexamethylene-diisocyanate in mixture with the 2,6,4-trimethylhexamethylene-
 diisocyanate isomer.

10 The compounds containing a hydroxyl group, capable of reacting with the isocyanic groups of the prepolymer, and an ethylenically unsaturated group, necessary to convert the polyisocyanic prepolymer into an oligo-urethane with terminal unsaturation, have the general
 15 formula:



where 'R' is hydrogen or methyl, and X is hydroxyalkyl radical, preferably 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl or 4-hydroxybutyl.

20 As ionizable diols, those can be employed which are able to give to the polyurethanic macromolecule a preferably anionic charge, because in this case finished products are obtained which are compatible with auxiliary substances, pigments, dyes and aqueous dispersions of
 25 different nature (for instance, acrylic, vinylic, butadieneacrylonitrilic etc.) nearly all of them of anionic nature.

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As ionizable diols, those can be employed which contain a free carboxylic group, preferably if it is linked with the same carbon atom carrying the two hydroxyl groups, for instance the dimethylolacetic, 5 dimethylolpropionic and dimethylolbutyric acids.

Furthermore those compounds can be employed which contain at least two hydroxyl groups and a carboxylic group that is not linked with the same carbon atom, such as the products of semiesterification of triols with bi-10 carboxylic aliphatic anhydrides.

As salification agents of the free carboxylic groups statistically distributed in the oligo-urethane chain, use can be made of both inorganic bases such as sodium and ammonium hydroxide, and, preferably, tertiary 15 amines or alkanolamines such as triethylamine, dimethyl-ethanolamine, and methyl-diethanolamine.

However, according to the present invention, dispersions may be obtained having cationic character by utilizing as ionizable diols the already known tertiary 20 alkyl-dialkanolamines, such as methyldiethanolamine, butyldiethanolamine, methyldiisopropanolamine, and by successively effecting salification of the tertiary nitrogen atom by means of organic and/or inorganic acids, such as hydrochloric, phosphoric, formic, lactic, and 25 acetic acids.

The salification of the oligo-urethane, either of potentially anionic or cationic kind, can be carried out by simple addition of the salification agent as such or

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dissolved in water and/or a suitable solvent at a temperature of about 90°C. Should the oligo-urethane have too high a viscosity at such temperature, dilution thereof may be carried out, before the salification, by means of 5 a solvent which can be preferably mixed with water and have a boiling temperature lower than that of water, so that it can be removed by distillation.

The necessary amount of solvent does not usually exceed one fifth of the weight of the oligo-urethane. 10 The preferred solvents are acetone, methyl-ethylketone, and tetrahydrofuran.

When the salification has been carried out, prior to possible dilution in organic solvent as above described, the oligo-urethane can be diluted in any ratio with water. 15 Therefore the water dispersion is proceeded with in order to obtain a content of non-volatile substance that is variable according to the content of the ionic groups, generally from 20 to 60% by weight, more preferably from 30 to 50% by weight, after having removed by distillation 20 the possible organic solvent that had been previously employed.

Then the unsaturated oligo-urethane, dissolved or dispersed in water as above described, can be polymerized, according to known techniques of bulk or semi-batch 25 polymerization. The polymerization is carried out by using a generator of free radicals, of organic peroxide or hydroperoxide kind, such as benzoyl peroxide, dicumyl

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peroxide, ter-butyl-hydroperoxide, cumene hydroperoxide, p-methane hydroperoxide, or sodium, potassium, or ammonium persulfate, used alone or together with a reducing agent such as sodium metabisulfite or sodium-
5 formaldehyde-sulfoxylate.

The polymerization temperature can be from 10° to 100°C, depending on the kind of initiator or of the initiator-reducing agent. The preferred polymerization temperature is from 50° to 70°C.

10 By carrying out the polymerization of oligo-urethanes containing at least two unsaturated terminal groups, reticulated tridimensional macromolecular structures are formed. If desired, the reticulation degree can be regulated at will, by carrying out the
15 polymerization in the presence of other mono- or poly-functional ethylenically unsaturated monomers. These can be added to the reaction bulk either during the transformation of the polyisocyanic prepolymer into unsaturated oligo-urethane or to the aqueous dispersion thereof. In
20 both cases the addition of the comonomers does not present any drawback until the amount thereof constitutes about 40% by weight, calculated on the oligo-urethane, calculated as dry, owing to the stabilizing action of the present ionic centers, that is comparable to a
25 surfactant action.

Examples of monofunctional ethylenically unsaturated monomers that can be utilized are methyl, ethyl, and butyl, acrylates and methacrylates, vinyl esters such as

13.

vinyl acetate and propionate, and vinylaromatic compounds such as styrene, α -methyl-styrene, and vinyltoluene.

Examples of polyfunctional ethylenically unsaturated monomers are trimethylpropane-triacrylate and trimethacrylate, pentaerythrytol triacrylate and trimethacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate and dimethacrylate, diethylene glycol diacrylate, and tetraethylene glycol diacrylate.

The final aqueous dispersions, obtained according to the present invention, are stable for a long time with complete lack of surfactant and/or colloidal protectors, are practically odourless, and consist of polymeric particles with average diameters variable within large limits, depending on the amount of the contained ionic centers, which can be numerically expressed in milliequivalents (meq) per 100 g of polymer, considered as dry. These values can vary from 10 to 60 meq/100 g of dry substance, preferably from 20 to 40 meq/100 g of dry substance.

Because of the ionic nature of the polymer, such dispersions are sensitive to electrolytes.

A possible stabilization thereof can be induced by surfactant and/or colloidal protectors of non-ionic kind, such as ethoxylated derivatives of higher fatty alcohols or alkylphenols. The use of ionic surfactants must, of course, take into account the cationic or anionic nature

of such dispersions.

By evaporation of the water the aqueous dispersions of the invention give rise to the forming of films of various hardness, flexibility and elasticity depending on the great variability of utilizable starting materials and on their formulative flexibility, which allows considerable variation in providing "hard" and "soft" segments of the finished polyurethane.

The aqueous dispersions of the invention can be advantageously employed as aqueous polymeric dispersions in coatings for wood, paper and metal, in the treatment of textiles, in the finishing of skins, and as adhesives, binders for fibrous materials, and dressings for fiber glass.

The invention will be further described with reference to the following illustrative Examples.

Example 1

Into a reactor provided with a stirrer and a cooler and kept under an atmosphere of dry nitrogen, dipped in an oil bath with temperature regulation, were fed in the following order: 241.87 g of a polyester obtained from adipic acid, ethylene glycol and 1,4-butanediol having an average molecular weight of about 1940 at reduced residual acidity (acidity number 0.2 mg KOH/g), 13.4 g of dimethylolpropionic acid and 66.56 g of toluene-diisocyanate 80/20 (mixture of 80% by weight of 2,4-isomer and 20% of 2,6-isomer).

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The reaction bulk, after having remained under stirring at 60°C for about 30 minutes, was heated to 80°C and kept at this temperature until the content of free isocyanic groups was about 5.2% by weight.

5 Then the atmosphere of dry nitrogen was replaced by dry air and 36.54 g of 2-hydroxyethylacrylate were fed in all at once. The reaction was carried out at 90°C until the disappearance of the free isocyanic groups occurred, which was determined by means of IR spectro-
10 photometry. Salification of the melted oligo-urethane was then effected by addition of 7.13 g of dimethylethan-olamine, followed by dispersion thereof in 548 g of de-ionized water.

The nitrogen atmosphere was then restored and the
15 dispersion thermostated at 65°C. Over a period of two hours 14.62 g of an aqueous solution of ter-butylhydroperoxide at 10% by weight were added dropwise and, at the end of the addition thereof, the dispersion was maintained at 65°C for a further hour.

20 The final dispersion had a white milky (lactescent) aspect, a content of solids of 39% by weight and a content of anionic groups of about 27 meq/100 g of dry substance.

By evaporation of the water at room temperature
25 there was formed a transparent, colourless, moderately flexible film, that was insoluble in acetone, dimethyl-formamide, and trichloroethylene.

Example 2

By following the same procedure as described in example 1, a polyurethanic dispersion was prepared, that was formulated as follows:

5	Polyester of example 1	251.55 g
	dimethylolpropionic acid	13.40 g
	toluenediisocyanate 80/20	60.03 g
	2-hydroxypropylacrylate	29.92 g
	dimethylethanolamine	7.13 g
10	ter-butylhydroperoxide (solution at 10% by weight)	14.48 g
	deionized water	543.04 g

The content of free isocyanic groups of the poly-isocyanic prepolymer was 4.1% by weight.

15 The final dispersion had a content of solids of 39.2% and a content of anionic groups of about 27.6 meq/100 g of dry substance; its colour was milky (lactescent) and its viscosity low.

20 A film, obtained by evaporation of the water, was colourless, more flexible than that of example 1, and was insoluble in organic solvents.

Such a dispersion, added with conventional thickeners, dyes and additives, used in the common acrylic emulsions, can be employed as an adhesive layer in the 25 manufacture of imitation leather obtained by the so-called "transfer" method. The obtained product was characterized by a high adhesion of the polyurethanic

layer to the textile support, of agreeable hand softness, and high resistance to solvents and washings.

Example 3

By following the same procedure as described in
5 example 1, a polyurethanic dispersion was prepared, that
was formulated as follows:

	polyester of example 1	263.16 g
	dimethylolpropionic acid	14.74 g
	hexamethylenediisocyanate	57.96 g
10	butanediolmonoacrylate	28.55 g
	dimethylethanolamine	7.84 g
	ter-butylhydroperoxide (solution at 10% by weight)	14.89 g
	deionized water	558.37 g

15 The content of free isocyanic groups of the poly-isocyanic prepolymer was 3.7% by weight.

The final dispersion had a content of solids of about 39.1% and a content of anionic groups of about 29.5 meq/100 g of dry substance.

20 A film, obtained by evaporation of the water, was colourless, flexible and insoluble in organic solvents.

The dispersion can be advantageously employed in the light finishing of quality skins, since it confers high resistance against various wet and dry abrasions, with
25 an excellent maintenance of the colour tonality even after exposure to the sun and U.V. radiation for a long time.

Example 4

By following the same procedure as described in example 1, a polyurethanic dispersion was prepared, that was formulated as follows:

5	polyester of example 1	263.16 g
	dimethylolpropionic acid	14.74 g
	trimethylhexamethylenediisocyanate	72.45 g
	2-hydroxyethylacrylate	25.74 g
	dimethylethanolamine	7.84 g
10	ter-butylhydroperoxide (solution at 10% by weight)	15.35 g
	deionized water	575.89 g

The content of free isocyanic groups of the poly-isocyanic prepolymer was 3.7% by weight.

15 The final dispersion had a content of solids of about 39.2% and a content of anionic groups of 28.6 meq/100 g of solids.

A film, obtained by evaporation of the water, was colourless, flexible and insoluble in organic solvents.

20 Example 5

By following the same procedure as described in example 1, a polyurethanic dispersion was prepared, that was formulated as follows:

	polyester of example 1	251.55 g
25	dimethylolpropionic acid	13.40 g
	hexamethylenediisocyanate	57.96 g

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2-hydroxypropylmethacrylate	33.12 g
dimethylethanolamine	7.13 g
ter-butylhydroperoxide (solution at 10% by weight)	14.52 g
5 deionized water	544.74 g

The content of free isocyanic groups of the poly-isocyanic prepolymer was 4.3% by weight.

The final dispersion had a content of solids of 39.2% and a content of anionic groups of 27.5 meq/100 g
10 of solids.

A film, obtained by evaporation of the water, was colourless, with good mechanical characteristics and insoluble in organic solvents.

Example 6

15 By following the same procedure as described in example 1, a polyurethanic dispersion was prepared, that was formulated as follows:

polyester of example 1	251.55 g
dimethylolpropionic acid	13.40 g
20 isophoronediisocyanate	76.06 g
2-hydroxyethylacrylate	26.68 g
dimethylethanolamine	7.13 g
ter-butylhydroperoxide (solution at 10% by weight)	15.00 g
25 deionized water	562.18 g

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The content of free isocyanic groups of the poly-isocyanic prepolymer was 4.1% by weight.

The final dispersion had a content of 39.2% of solids and a content of anionic groups of 26.7 meq/100 g
5 of solids.

A film, obtained by evaporation of the water, was colourless, and insoluble in organic solvents.

The dispersion can be applied in a similar manner to that of example 3, in the finishing of full bloom of
10 skins.

CLAIMS

1. A process for producing stable aqueous dispersions of polyurethanes containing in the macromolecule hydrophilic ionic groups, as internal surfactants, either of anionic or cationic nature, which are present in amounts of 5 10 - 60 meq/100 g of dry polyurethane, the process being characterised by the following steps:

- a) a mixture of a diol containing ionizable groups, which can be converted into hydrophilic anionic or cationic groups, and of an essentially linear 10 macroglycol, having a molecular weight of from 500 to 5000, of polyol-polyether and/or polyol-polyester type, is reacted at a temperature not higher than 100°C with an excess of a diisocyanate, thereby obtaining a prepolymer containing free 15 isocyanic groups;
- b) the polyisocyanic prepolymer is then converted into oligo-urethane containing vinyl terminal unsaturated groups, by reaction with a compound 20 containing hydroxyl radicals, which are reactive towards the isocyanic group, and having the general formula:



where R is H or CH_3 , and X is a hydroxyalkyl radical;

- c) the obtained oligo-urethane is subjected to salification in order to convert the ionizable groups into hydrophilic cations or anions, respectively of quaternary ammonium type or of carboxylic, sulphonic or phosphonic group type;
- d) the oligo-urethane containing the hydrophilic cationic and anionic groups is subjected to polymerization treatment of the terminal unsaturated groups, in an aqueous dispersion, in the presence of a radical catalyst at a temperature not higher than 100°C, so as to obtain an aqueous dispersion of polyurethane having a pre-established reticulation degree, that can be regulated by means of an optional addition of comonomer present in the polymerization step.
2. A process as claimed in claim 1, characterised in that use is made of a diol containing a carboxylic group that is successively salified by a tertiary amine.
3. A process as claimed in claim 1, characterised in that use is made of a diol containing a tertiary aminic group, that is successively converted into a quaternary ammonic cation by salification.
4. A process as claimed in any of claims 1 to 3, characterized in that the reaction between polyisocyanic prepolymer and hydroxylated unsaturated compound is carried out at a temperature from 80° to 120°C.

5. A process as claimed in any of claims 1 to 4, characterized in that the ratio between the -NCO groups of the polyisocyanic prepolymer and the -OH groups of the hydroxylated unsaturated compound is
5 from 0.5:1 to 1.1:1.
6. A process as claimed in any of claims 1 to 5, characterized in that the molar ratio between the isocyanic groups and the sum of the hydroxyl groups of the macroglycol and the diol is from 1.2:1
10 to 2:1.
7. An aqueous dispersion of a polyurethane having a reticulated structure, having hydrophilic ionic groups, present in amounts of 10-60 meq/100 g of polymer, obtained at a concentration of from 20
15 to 60% by weight of dry polymer, according to the process of claim 1.